

Article

Wet-Chemical Synthesis of TiO₂/PVDF Membrane for Energy Applications

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Abstract: To satisfy the ever-increasing energy demands, it is of the utmost importance to develop electrochemical materials capable of producing and storing energy in a highly efficient manner. Titanium dioxide (TiO₂) has recently emerged as a promising choice in this field due to its non-toxicity, low cost, and eco-friendliness, in addition to its porosity, large surface area, good mechanical strength, and remarkable transport properties. Here, we present titanium dioxide nanoplates/polyvinylidene fluoride (TiO₂/PVDF) membranes prepared by a straightforward hydrothermal strategy and vacuum filtration process. The as-synthesized TiO₂/PVDF membrane was applied for energy storage applications. The fabricated TiO₂/PVDF membrane served as the negative electrode for supercapacitors (SCs). The electrochemical properties of a TiO₂/PVDF membrane were explored in an aqueous 6 M KOH electrolyte that exhibited good energy storage performance. Precisely, the TiO₂/PVDF membrane delivered a high specific capacitance of 283.74 F/g at 1 A/g and maintained capacitance retention of 91% after 8000 cycles. Thanks to the synergistic effect of TiO₂ and PVDF, the TiO₂/PVDF membrane provided superior electrochemical performance as an electrode for a supercapacitor. These superior properties will likely be used in next-generation energy storage technologies.

Keywords: TiO₂ nanoplates; PVDF; wet-chemical; negative electrode; energy storage



Citation: Saleem, M.; Albaqami, M.D.; Bahajjaj, A.A.A.; Ahmed, F.; Din, E.; Arifeen, W.U.; Ali, S. Wet-Chemical Synthesis of TiO₂/PVDF Membrane for Energy Applications. *Molecules* **2023**, *28*, 285. <https://doi.org/10.3390/molecules28010285>

Academic Editor: David G. Churchill

Received: 2 December 2022

Revised: 21 December 2022

Accepted: 23 December 2022

Published: 29 December 2022



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1. Introduction

The constant consumption of conventional fossil fuels and the resulting increase in environmental problems have made the development of low-carbon emissions and environmentally friendly methods of energy storage an urgent necessity [1,2]. Supercapacitors (SCs) have led to their widespread consideration as renewable sources due to the favorable electrochemical performance of rapid charging/discharging methods, high power density, and extended cycle stability [3,4]. Depending on their charge storage mechanism, SCs are classified as electric double-layer capacitors (EDLCs) or pseudocapacitors (PCs) [5]. Compared to EDLCs, PCs can offer diverse redox states and achieve high specific capacitance because of the reversible redox reactions at the electrode/electrolyte interface and on the active materials' surfaces [6].

Electrode materials can significantly affect the use of such energy storage devices for practical applications [7,8]. Widespread functional materials, including activated carbon [9], carbon nanotubes [10], graphene [11], and transition metal oxides [12,13] have significant potential because of their stability and remarkable electrochemical performance. However,

most commercial carbon materials have poor capacitance because of their formless morphology, hindered aggregation, and ineffective electrical double-layer capacitive reactions. Among various transition metal oxides, titanium oxides are considered ideal electrode materials for charge storage due to their stable structures and appropriate operating potential. Numerous studies have shown that titanium oxides with a layer structure and linked framework might be advantageous for rapidly inserting aqueous ions by providing favorable transport and distinctive pseudocapacitance [14,15].

Among numerous transition metal oxides, titanium dioxide (TiO_2) is one of the most extensively employed semiconductors and photocatalysts in dye-sensitized solar cells [16]. High surface-to-volume ratio, abundant availability, good conductivity, high energy density, and outstanding light absorption properties make TiO_2 a valuable material for SC electrode [17]. In particular, nanostructured TiO_2 is increasingly garnering attention as an electrode material in SCs because of its large specific surface area and low cost compared with other metal oxides. For instance, Lee et al. [18] presented mesoporous MnO_2 microparticles mixed with TiO_2 nanoparticles, and the $\text{TiO}_2/\text{MnO}_2$ composite electrode delivered a specific capacitance of 279 F/g at 10 mV/s with 73.4% capacitance retention after 5000 cycles. However, TiO_2 's significant limitations, such as its limited electrical conductivity and sluggish ion diffusion, restrict its effectiveness [19]. Therefore, to fabricate low-cost and practically applicable SCs based on TiO_2 , strategies that have the potential to improve the performance of TiO_2 are in great demand. Alternatively, TiO_2 's good chemical stability and eco-friendliness make it a promising material for the synthesis of composite electrodes in numerous charge storage devices.

Since polymer membranes offer considerable electrochemical stability and are simple to produce, such membranes have been used in SCs. To improve the membrane's physical, electrical, and mechanical characteristics, polymer composite membrane preparation is a technology added to boost conductivity at ambient temperature [20]. Among several polymers, polyvinylidene fluoride (PVDF) is an exceptionally non-reactive thermoplastic fluoropolymer synthesized via the polymerization of vinylidene difluoride. It has a good resistance against the range of solvents (including basic and acidic ones) and, compared to other fluoropolymers, possesses a low density [21].

Therefore, considering the widespread application of TiO_2 nanoplates due to their excellent characteristics that lead to enhanced chemical and thermal stability. In this work, the preparation of TiO_2 nanoplates/PVDF membrane (denoted as TiO_2/PVDF) was reported using a straightforward hydrothermal process. Because of its membrane-like structure, the composite material has supported the development of an effective electrode for SC applications. Experimental evidence exhibit that the TiO_2/PVDF electrode has the advantageous characteristics of a high specific surface area and rapid charge transfer. Thus, the TiO_2/PVDF electrode showed a maximum specific capacitance of 283.74 F/g at a current density of 1 A/g. In addition, the TiO_2/PVDF electrode retained 91% of its capacitance after 8000 cycles, indicating its viability for use in the emerging field of energy storage.

2. Results and Discussion

Figure 1 provides a schematic illustration of the synthesis procedure for TiO_2/PVDF membranes using a straightforward and facile hydrothermal strategy. During the fabrication method, titanium tetra-*n*-butoxide was converted into TiO_2 nanoplates, which are then used to embellish the TiO_2/PVDF membrane. As a result, a TiO_2/PVDF membrane was fabricated with the ease of a simple vacuum filtration process.

FE-SEM was used to investigate the structure and morphology of the as-synthesized TiO_2 product. Low and high magnification SEM images (Figure 2a–c) exhibit the homogeneous dispersion of TiO_2 nanoplates with an average size of 79 nm, demonstrating the outstanding TiO_2 nanoplates adhesion and effective grafting on PVDF membrane. Simultaneously, particle size reduction substantially enhanced the specific surface area of TiO_2 and the number of its active sites in solution [22]. Uniform dispersion of these TiO_2 nanoparticles was necessary to maximize the contact area between TiO_2 nanoparticles and PVDF.

As a result, the TiO_2/PVDF membrane with tiny and evenly dispersed TiO_2 nanoparticles was expected to have a wide range of applications in the field of electrochemical energy storage. It should be noted that the morphology of the TiO_2/PVDF remained almost same of like TiO_2 due to the small amount of the PVDF. These TiO_2 nanoplates combined to form a unique porosity network which established wide channels for the fast transport of K^+ and OH^- ions. Consequently, electrolyte ions may readily interact with the surface of most nanoplates. This decreased the ion diffusion distance, which ultimately resulted in an improvement in the electrochemical performance.

Figure 3a displays the X-ray diffraction (XRD) patterns of the as-synthesized TiO_2 . All diffraction peaks were strong, indicating that the sample had high crystallinity. The XRD analysis showed that the TiO_2 pattern was accurately indexed with the standard tetragonal rutile phase (JCPDS Card No. 21-1276) [23]. The thermogravimetric analysis (TGA) was used to study the thermal stability of TiO_2 from 0 to 1000 °C in an air environment at a ramping rate of 5 °C/min. Figure 3b exhibits that the TiO_2 nanoplates lost just 8.3% of their weight because of the absorbed water process when subjected to temperatures between 25 and 200 °C. TiO_2 nanoplates showed a weight loss of 15.78% when subjected to temperatures between 200 and 390 °C. The reduction of -OH groups on the surface of the TiO_2 nanoplates was primarily responsible for this result. Furthermore, the weight of the TiO_2 nanoplates decreased by 21.4% when heated to temperatures ranging from 390 to 600 °C [24]. The buoyancy effect of TGA equipment may account for the modest gain in weight seen [25,26]. Finally, stability up to 800 °C demonstrated the suitability of TiO_2 for high-temperature applications, where conventional materials would degrade. Fourier transformed infrared (FTIR) was also performed to verify the composition and bonding structure of TiO_2 . Figure 3c shows that TiO_2 had a strong band at 670 cm^{-1} , which was associated with the stretching vibration of Ti-O [27], and the peaks at 1534 and 1736 cm^{-1} can be related to the stretching vibration of H-O-H. Additionally, the peaks located at 2872 and 2969 cm^{-1} may be attributed to the C-H stretching vibration [28], and a peak at 3020 cm^{-1} can be associated with O-H stretching vibration, indicating that the utilization of TiO_2 might increase the hydrophilicity of the membrane [29].

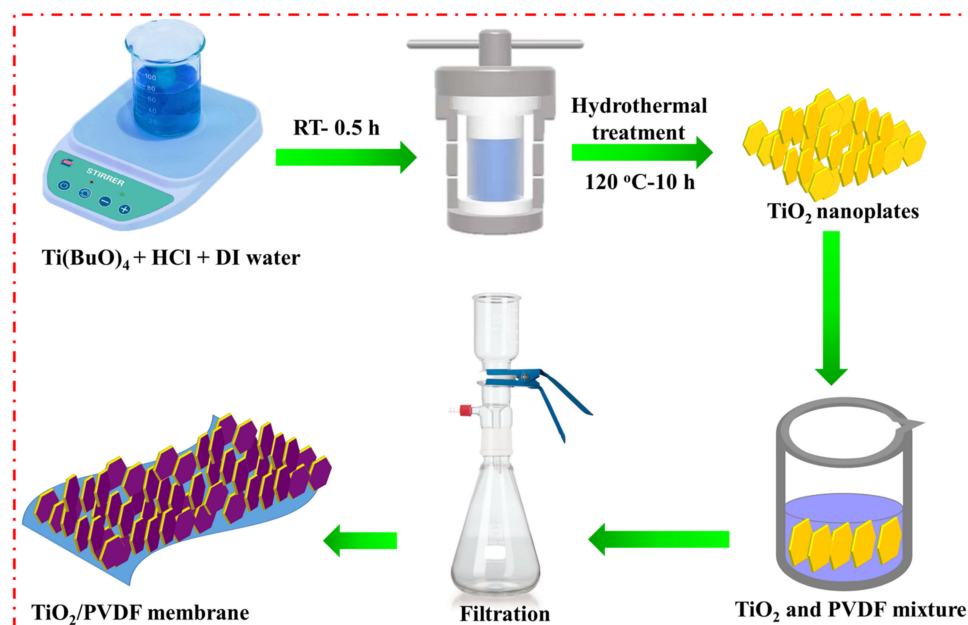


Figure 1. Schematic diagram of the synthesis strategy of TiO_2/PVDF membrane.

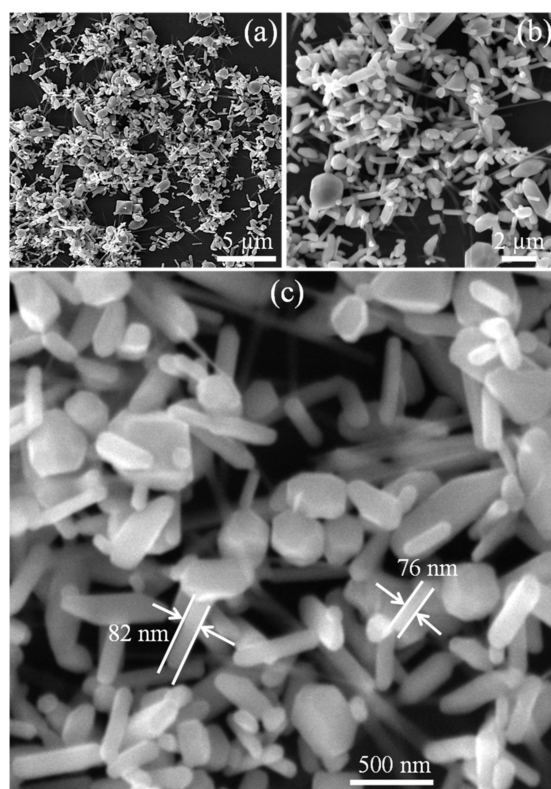


Figure 2. SEM images of TiO_2 at; (a,b) Low-magnification; (c) High-magnification.

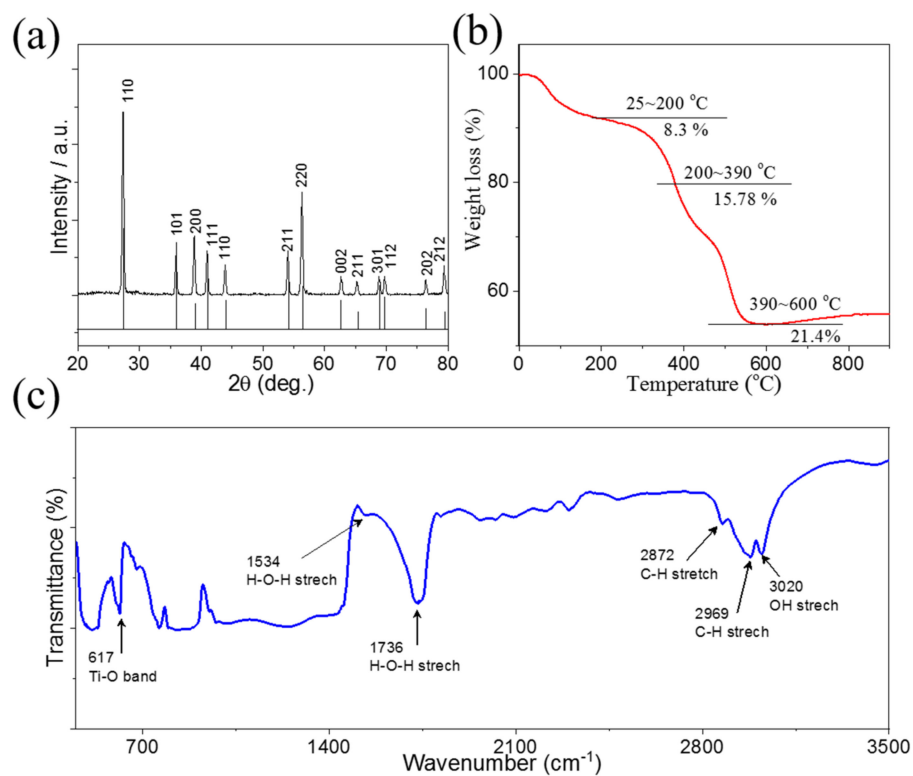


Figure 3. (a) XRD patterns of TiO_2 ; (b) TGA curve of TiO_2 ; (c) FTIR spectra.

The N_2 adsorption/desorption isotherms of TiO_2 are shown in Figure 4a, which exhibit a hysteresis loop at $P/P_0 > 0.7$ and confirm a typical type IV adsorption behavior, indicating that TiO_2 likely possesses a mesoporous structure. Furthermore, when the

relative pressure $P/P_0 > 0.8$, the adsorption/desorption isotherm was steep because, during cohesion and evaporation, the relative pressure was centered, suggesting that the TiO_2 exhibited mesoporous characteristics. The BET-specific surface area of TiO_2 was calculated to be $17.613 \text{ m}^2/\text{g}$ [28].

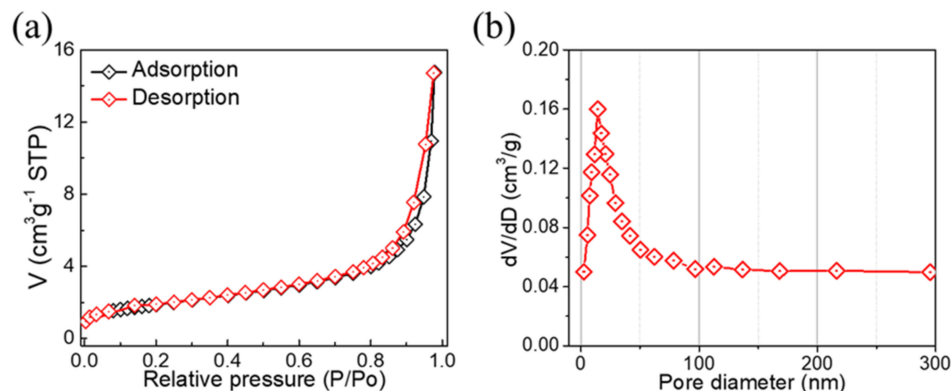


Figure 4. (a) N_2 adsorption/desorption isotherm; (b) Typical pore size distribution of TiO_2 .

Figure 4b depicts the BJH pore size distribution curve, and an average pore size of 23.4 nm was observed, indicating the presence of sizable pores. Because of the large pore size and increased specific surface area, there would be more electroactive sites and easier access for the electrolyte ions. This would improve the electrode materials' electrochemical performance for storing charge [30].

The electrochemical performance of the TiO_2/PVDF membrane for the energy storage device as a supercapacitor electrode was investigated in a three-electrode setup, as shown in Figure 5. The CV profiles of the TiO_2/PVDF electrode were measured in the potential window of -0.6 to 0.0 V and at various scan rates ranging from 5 to 50 mV/s , and the results are presented in Figure 5a. The nearly-rectangular CV profiles of the TiO_2/PVDF electrode suggested that the electrode material exhibits exceptional capacitive performance and high-rate capability. The CV profiles possess remarkable stability, even at high scan rates, demonstrating the low polarization resistance of the TiO_2/PVDF electrode [31]. In the CV profiles, the robust current response is another demonstration of the outstanding charge storage capacity and quick electrolyte ion accessibility. When the scan rate was low, both the inner and outer surfaces of the sample could be utilized as charge storage. However, when scan rates were higher, the diffusion of OH^- ions was more likely to occur exclusively on the surface, and only a negligible fraction of OH^- ions could insert into the inner surface. This phenomenon demonstrates that the porous characteristics of the TiO_2/PVDF membrane allow it to accommodate the OH^- ions [32–34].

Figure 5b exhibits the GCD profiles of TiO_2/PVDF electrode at different current densities from 1 and 30 A/g , where symmetric GCD profiles are attributed to the pseudo-capacitive characteristics of the electrode. Also, each GCD profile shows great symmetry without a discernible plateau, indicating high Coulombic efficiency and good reversibility. Figure 5c depicts the specific capacitance (C_{sp} (F/g)) of the TiO_2/PVDF electrode (according to Equation (1)) from the GCD profiles at current densities ranging from 1 to 30 A/g . The TiO_2/PVDF electrode delivered a C_{sp} of as high as 283.74 , 255.09 , 233.41 , 216.65 , 190.18 , and 174.94 F/g at 1 , 3 , 5 , 10 , 20 , and 30 A/g , respectively. After increasing the current density from 1 to 30 A/g , the TiO_2/PVDF electrode showed a capacitance retention of 61.6% , which demonstrated a remarkable rate capability at high current density. The C_{sp} of the electrode remained as a maximum of 174.94 F/g even though the current density was increased to 30 A/g (capacitance retention of $\sim 61.6\%$). An EIS test was also performed to understand the impedance of the TiO_2/PVDF electrode, and the Nyquist plot is shown in Figure 5d. The equivalent series resistance (R_s) of the electrode is characterized in the high-frequency zone by the intercept at the real axis, which was $\sim 0.84 \Omega$ (includes the internal resistance of

electrode material and electrolyte resistance). The small value of R_s implies that there is excellent electrical conductivity between the electrode material and the current collector. The radius of a semi-circle corresponds to charge-transfer resistance (R_{ct}), which is $\sim 0.99 \Omega$. In the low-frequency zone, the quasi-vertical line represents the Warburg impedance Z_w of the electrolyte diffusion. The slope of the line is associated with the ionic diffusion of the electrolyte to the electrode surface. The EIS curve was fit using an equivalent electrical model created with the help of ZSimpWin. This model included the R_{ct} , R_s , and constant phase element (CPE). These values can be seen in the inset of Figure 5d [35–37]. It seems that TiO_2/PVDF electrode with small R_s and R_{ct} , became the most electrochemically active compared to MoS_2 ($R_s \sim 4 \Omega$ and $R_{ct} \sim 4.3 \Omega$) [35], b-TiO_2 ($R_s \sim 1.60 \Omega$ and $R_{ct} \sim 15.3 \Omega$) [38] and ICS-TiO_2 ($R_s \sim 7.5 \Omega$ and $R_{ct} \sim 11.3 \Omega$) [39] electrodes.

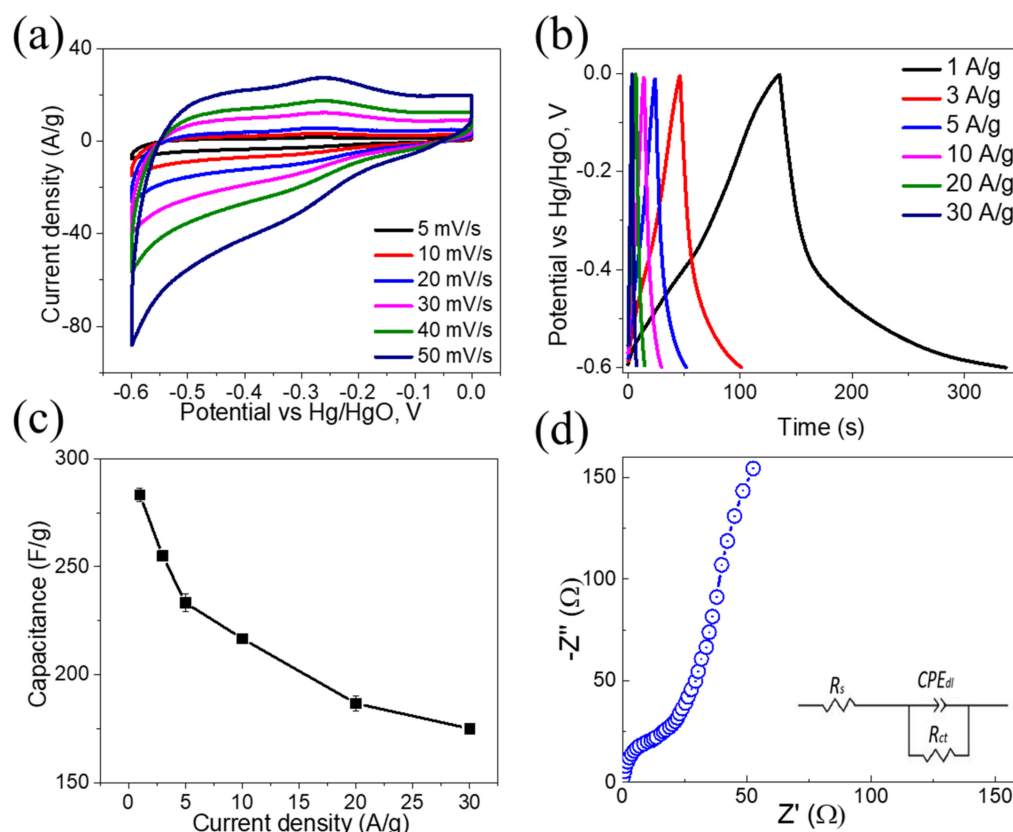


Figure 5. Electrochemical measurements of a TiO_2/PVDF membrane electrode in the aqueous electrolyte; (a) CV profiles at different scan rates; (b) GCD profiles at different current densities; (c) Specific capacitance versus current density; (d) Nyquist plot.

The cycling stability analysis is an essential parameter for SC electrode materials. Figure 6a shows the cycling stability test of the TiO_2/PVDF electrode, which was carried out by continuously operating it for 8000 GCD cycles at a current density of 10 A/g. The TiO_2/PVDF electrode retained a capacitance of 91% after 8000 cycles, demonstrating the extremely high stability and excellent energy storage capabilities of the TiO_2/PVDF electrode throughout GCD cycles. This enhanced electrochemical performance of the synthesized TiO_2/PVDF electrode in an aqueous electrolyte may be due to the membrane-like morphology of the TiO_2/PVDF electrode and its increased electrical conductivity [40]. The importance of the TiO_2/PVDF electrode can be better understood by comparing its electrochemical performance with that of different composites.

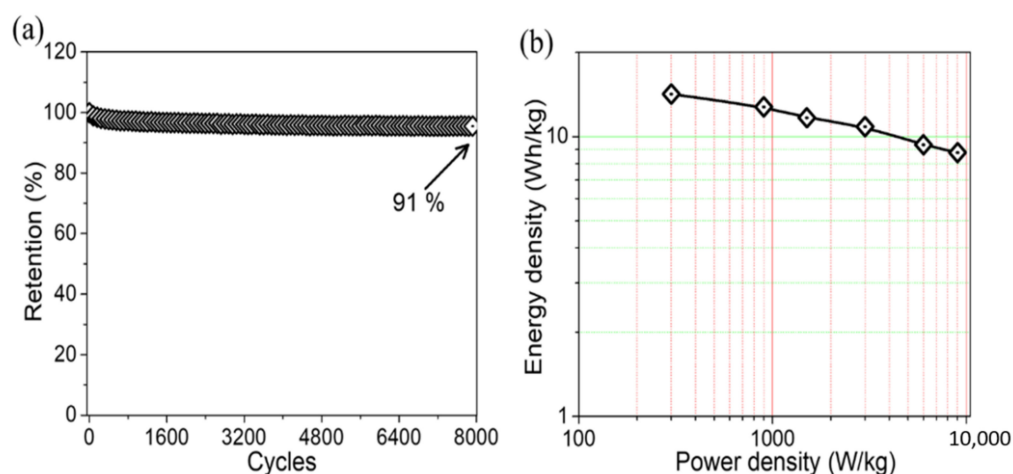


Figure 6. (a) Cycling performance of the TiO₂/PVDF electrode; (b) Energy density versus power density.

Table 1 shows the overall performance of the TiO₂/PVDF electrode compared to that of previously published related electrodes in terms of specific capacitance and cycling stability, which shows the superior performance of the TiO₂/PVDF electrode. To analyze the overall performance of SC, the power density vs. energy density (Ragone plots) for the TiO₂/PVDF electrode was calculated according to Equations (2) and (3) and displayed in Figure 6b. The estimated E and P of the TiO₂/PVDF electrode were 14.78, 12.76, 11.68, 10.84, 9.34, and 8.76 Wh/kg and 300.24, 900.72, 1501.2, 3002.4, 6004.8, and 9007.2 W/kg, respectively. Since E is directly dependent on specific capacitance, a higher specific capacitance in the TiO₂/PVDF electrode led to a higher E. A maximum energy density of 14.18 Wh/kg was achieved while maintaining a power density of 300.24 W/kg. The experimental data demonstrates that TiO₂/PVDF membrane was a viable electrode material for SCs.

Table 1. A comparison table of the electrochemical performance of previously published works with the as-prepared TiO₂/PVDF membrane for supercapacitor applications.

Sr. No.	Electrode Material	Electrolyte	Specific Capacitance (GCD/CV)	No. of Cycles (n)	Capacitance Retention (%)	Ref.
1	TiO ₂ /PVDF membrane	KOH	283.74 F/g (1 A/g)	8000	91	This work
2	CB)/TiO ₂	H ₂ SO ₄	236 F/g (10 mV/s)	10,000	90.3	[41]
3	Fe-TiO ₂ /C nanofibers	KOH	137 F/g (5 mV/s)	-	-	[42]
4	TiO ₂ -graphene composites	KOH	84 F/g (10 mV/s)	1000	87.5	[43]
5	N-TiO ₂ /NG	Na ₂ SO ₄	205.1 F/g (1 mV/s)	5000	78.8	[44]
6	BC-G-TiO ₂	H ₂ SO ₄	250.8 F/g (2 A/g)	100	84.4	[45]
7	TiO ₂ -activated carbon	Na ₂ SO ₄	92 F/g (5 mV/s)	5000	89.9	[46]
8	TiO ₂ -CNT	H ₂ SO ₄	110 F/g (0.05 mA/cm ²)	-	-	[47]
9	rGO/TiO ₂ NR/rGO	Na ₂ SO ₄	114.5 F/g (5 mV/s)	4000	85	[48]
10	TiO ₂ -carbon NFs	KOH	106.57 F/g (1A/g)	2000	84	[16]

3. Experimental Section

3.1. Synthesis of TiO₂ Nanoplates

To fabricate TiO₂ nanoplates, a hydrothermal process was applied to titanium (IV) butoxide (Ti(BuO)₄) (Sigma-Aldrich), hydrochloric acid (HCl), ethanol, and deionized (DI) water. After adding Ti(BuO)₄ (4.8 g) to 15 mL of HCl, 12 mL of DI water was added. The resultant complex was agitated using a magnetic stirrer at room temperature (RT) for 30 min. The solution was then placed in an autoclave and heated in an oven at a temperature of

120 °C for reaction durations of 10 h. Then, the autoclave was left to cool at an ambient temperature naturally, and TiO₂ nanoplates were collected and rinsed with DI water.

3.2. Synthesis of TiO₂/PVDF Membrane

For the typical synthesis of TiO₂/PVDF membrane, a solution was prepared by dissolving PVDF in dimethylformamide (DMF) (containing PVDF powder of 0.1 g dissolved in 10 mL of DMF) and stirring it to completely dissolved PVDF. Then, 0.9 g of TiO₂ nanoplates were mixed in a PVDF/DMF solution. A hand-casting knife with a 150 µm gap was used to mix the slurry uniformly. Afterwards, the mixture was vacuum filtered through a mesh (0.45 µm), and the resulting TiO₂/PVDF membrane was collected on the filter paper. Finally, the TiO₂/PVDF membrane was washed with DI water to eliminate any residuals of the solvent and dried at 60 °C.

3.3. Physical Characterization of TiO₂/PVDF Membrane

To investigate the morphology of TiO₂, a field emission scanning electron microscope (FESEM, HITACHI SU8220, Hitachi High-Technologies, Tokyo, Japan) was used. The crystal structure was analyzed via an X-ray diffractometer (XRD, Philips X'Pert Pro Analytical, Philips, Singapore) using monochromatic radiation (Cu-Kα; = 0.15406 nm). The thermogravimetric analysis (TGA) measurement was carried out in an air environment at a 5 °C/min heating rate from room temperature to 1000 °C. Fourier transformed infrared (FTIR) spectra (Vector-22 spectrometer, Nicolet IS 10, Thermo Scientific, Waltham, MA, USA) was used. For the analysis of the surface area and pore size, Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) analytical curves with the (Micromeritics ASAP2460, Micromeritics, Shanghai, China) analyzer were acquired, respectively.

3.4. Electrochemical Characterization of TiO₂/PVDF Membrane

The electrochemical measurements were carried out with a three-electrode configuration using an electrochemical workstation (CHI 660E, Corrtest Instruments, Wuhan, China). The as-synthesized TiO₂/PVDF (1.5 × 2.5 cm²) membrane with a mass loading of 1.1 mg/cm² was used as a working electrode for Hg/HgO, and platinum wire was used as a reference and counter electrodes, respectively, in an aqueous electrolyte containing 6 M KOH. A cyclic voltammogram (CV) was performed over a potential window range of −0.6 to 0.0 V. Galvanostatic charge-discharge (GCD) was carried out over the same potential window range (−0.6 to 0.0 V) at varying current densities (1 to 30 A/g). The electrochemical impedance spectroscopy (EIS) was performed at frequencies ranging from 0.001 to 100 kHz at open circuit conditions with a 5-mV amplitude.

The following Equation (1) was used to determine the specific capacitance (C_{sp} (F/g)) of the TiO₂/PVDF membrane:

$$C_{sp} = \frac{1}{mv(V_f - V_i)} \int_{V_i}^{V_f} I dV \quad (1)$$

where $m(g)$ is the mass of active material, $v(V/s)$ is the scan rate, $I(A)$ is the applied current, and $\Delta V(V_f - V_i)$ is the potential window.

The following Equations (2) and (3) were used to calculate the energy density E (Wh/kg) and the power density P (kW/kg). Where C_{sp} is the electrode's specific capacitance and ΔV is the potential, t_d is the discharge time.

$$E = 0.139 C_{sp} \Delta V^2 \quad (2)$$

$$P = \frac{E}{t_d} \quad (3)$$

4. Conclusions

In summary, we have demonstrated TiO₂/PVDF membranes fabricated via a cost-effective and straightforward hydrothermal strategy and employed as electrode material for energy storage applications. The electrochemical investigations of the as-prepared TiO₂/PVDF electrode using a three-electrode configuration in an aqueous electrolyte exhibited exceptional performance and delivered a specific capacitance of 283.74 F/g at 1 A/g. The TiO₂/PVDF electrode retained a capacitance of 91% after 8000 cycles. Additionally, a maximum energy density of 14.18 Wh/kg of TiO₂/PVDF electrode was achieved while maintaining a power density of 300.24 W/kg. Our findings demonstrate that the TiO₂/PVDF electrode has the potential to deliver an adjustable electrochemical performance, which is a prerequisite for its commercialization and use in the development of state-of-the-art supercapacitors.

Author Contributions: Conceptualization, M.S., A.A.A.B., F.A. and S.A.; methodology, M.D.A., A.A.A.B., E.D. and W.U.A.; software, M.S., M.D.A., E.D. and S.A.; validation, M.S., M.D.A. and W.U.A.; formal analysis, M.D.A., A.A.A.B., F.A., E.D., W.U.A. and S.A.; investigation, A.A.A.B., F.A. and W.U.A.; data curation, E.D.; writing—original draft preparation, M.S., M.D.A. and F.A.; writing—review and editing, A.A.A.B. and E.D.; visualization, F.A.; supervision, W.U.A. and S.A.; project administration, S.A.; funding acquisition, M.D.A., A.A.A.B. and E.D. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by the Researchers Supporting Project Number (RSP-2021/267) King Saud University, Riyadh, Saudi Arabia.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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